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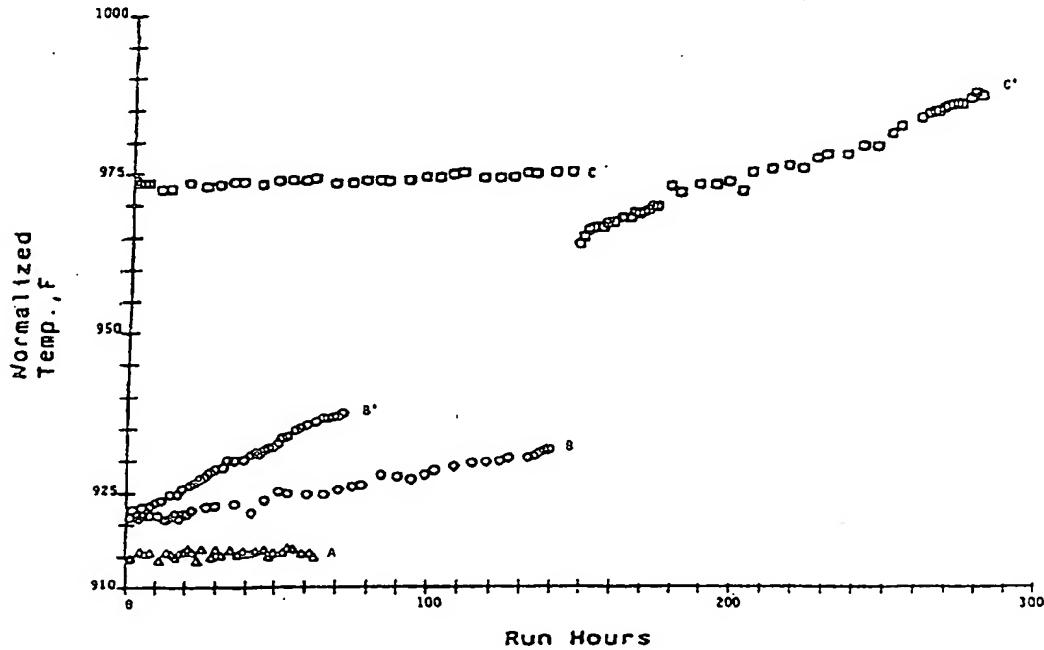
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(54) Title: ZEOLITE SSZ-42



(57) Abstract

The present invention relates to new crystalline zeolite SSZ-42 prepared by processes for preparing crystalline molecular sieves, particularly large pore zeolites, using an organic templating agent selected from the group consisting of N-benzyl-1,4-diazabicyclo[2.2.2]octane cations and N-benzyl-1-azabicyclo[2.2.2]octane cations.

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01

ZEOLITE SSZ-42

02

03

BACKGROUND OF THE INVENTION

04

05

Field of the Invention

06

07

The present invention relates to new crystalline zeolite SSZ-42 prepared using an N-benzyl-1,4-diazabicyclo[2.2.2]octane cation or N-benzyl-1-azabicyclo[2.2.2]octane cation templating agent, and hydrocarbon conversion processes using SSZ-42 as a catalyst.

12

13

State of the Art

14

15

In conventional usage the term "molecular sieve", refers to a material having a fixed, open-network structure, usually crystalline, that may be used to separate hydrocarbons or other mixtures by selective occlusion of one or more of the constituents, or may be used as a catalyst in a catalytic conversion process. The term "zeolite" refers to a molecular sieve containing a silicate lattice, usually in association with some aluminum, boron, gallium, iron, and/or titanium. In the following discussion and throughout this disclosure, the terms molecular sieve and zeolite will be used more or less interchangeably. One skilled in the art will recognize that the teachings relating to zeolites are also applicable to the more general class of materials called molecular sieves.

29

30

Natural and synthetic crystalline molecular sieves are useful as catalysts and adsorbents. Each crystalline molecular sieve is distinguished by a crystal structure with an ordered pore structure, and is characterized by a unique X-ray diffraction pattern. Thus, the crystal structure

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01 defines cavities and pores which are characteristic of the
02 different species. The adsorptive and catalytic properties
03 of each crystalline molecular sieve are determined in part
04 by the dimensions of its pores and cavities. Accordingly,
05 the utility of a particular molecular sieve in a particular
06 application depends at least partly on its crystal
07 structure.

08

09 Because of their unique sieving characteristics, as well as
10 their catalytic properties, crystalline molecular sieves are
11 especially useful in applications such as hydrocarbon
12 conversion, gas drying and separation. Although many
13 different crystalline molecular sieves have been disclosed,
14 there is a continuing need for new zeolites with desirable
15 properties for gas separation and drying, hydrocarbon and
16 chemical conversions, and other applications.

17

18 Crystalline aluminosilicates are usually prepared from
19 aqueous reaction mixtures containing alkali or alkaline
20 earth metal oxides, silica, and alumina. Crystalline
21 borosilicates are usually prepared under similar reaction
22 conditions except that boron is used in place of aluminum.
23 By varying the synthesis conditions and the composition of
24 the reaction mixture, different zeolites can often be
25 formed.

26

27 Organic templating agents are believed to play an important
28 role in the process of molecular sieve crystallization.
29 Organic amines and quaternary ammonium cations were first
30 used in the synthesis of zeolites in the early 1960s as
31 reported by R. M. Barrer and P. J. Denny in *J. Chem. Soc.*
32 1961 at pages 971-982. This approach led to a significant
33 increase in the number of new zeolitic structures discovered
34

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01 as well as an expansion in the boundaries of composition of
02 the resultant crystalline products.

03

04 Previously, products with low silica to alumina ratios
05 ($\text{SiO}_2/\text{Al}_2\text{O}_3 \leq 10$) had been obtained, but upon using the
06 organocations as components in the starting gels, zeolites
07 with increasingly high $\text{SiO}_2/\text{Al}_2\text{O}_3$, were realized. Some of
08 these materials are summarized by R. M. Barrer 1982,
09 *Hydrothermal Chemistry of Zeolites*, New York: Academic
10 Press, Inc.

11

12 Unfortunately, the relationship between structure of the
13 organocation and the resultant zeolite is far from
14 predictable, as evidenced by the multitude of products which
15 can be obtained using a single quaternary ammonium salt as
16 reported by S. I. Zones et al., 1989, *Zeolites: Facts,*
17 *Figures, Future*, ed. P. A. Jacobs and R. A. van Santen,
18 pp. 299-309, Amsterdam: Elsevier Science Publishers, or the
19 multitude of organocations which can produce a single
20 zeolitic product as reported by R. M. Barrer, 1989, *Zeolite*
21 *Synthesis*, ACS Symposium 398, ed. M. L. Occelli and H. E.
22 Robson, pp. 11-27, American Chemical Society.

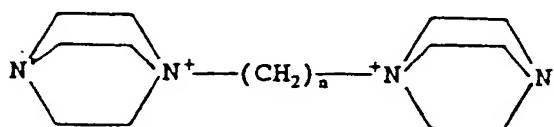
23

24 Thus, it is known that organocations exert influence on the
25 zeolite crystallization process in many unpredictable ways.
26 Aside from acting in a templating role, the organic cation's
27 presence also greatly affects the characteristics of the
28 gel. These effects can range from modifying the gel pH to
29 altering the interactions of the various components via
30 changes in hydration (and thus solubilities of reagents) and
31 other physical properties of the gel. Accordingly,
32 investigators have now begun to consider how the presence of
33 a particular quaternary ammonium salt influences many of
34

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01 these gel characteristics in order to determine more
02 rigorously how such salts exert their templating effects.
03

04 U. S. Patent No. 5,194,235, issued March 6, 1993 to Zones,
05 discloses the use of a templating agent known as
06 DABCO-C_n-diquat to prepare the zeolite SSZ-16. This
07 templating agent has the following formula:
08



13 wherein n is 3, 4 or 5.
14

15 In summary, a variety of templates have been used to
16 synthesize a variety of molecular sieves, including zeolites
17 of the silicate, aluminosilicate, and borosilicate families.
18 However, the specific zeolite which may be obtained by using
19 a given template is at present unpredictable. In fact, the
20 likelihood of any given organocation serving as an effective
21 template useful in the preparation of a molecular sieve is
22 conjectural at best. In particular, organocation templating
23 agents have been used to prepare many different combinations
24 of oxides with molecular sieve properties, with silicates,
25 aluminosilicates, aluminophosphates, borosilicates and
26 silicoaluminophosphates being well known examples.
27

28 SUMMARY OF THE INVENTION
29

30 In accordance with the present invention there is provided
31 a zeolite having a mole ratio of an oxide selected from
32 silicon oxide, germanium oxide and mixtures thereof to an
33 oxide selected from aluminum oxide, gallium oxide, iron
34 oxide, titanium oxide, boron oxide and mixtures thereof

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01 greater than about 10 and having the X-ray diffraction lines
02 of Table I.

03

04 The present invention also provides a zeolite having an
05 average pore size diameter greater than about 6 Angstroms
06 and having the X-ray diffraction lines of Table II.

07

08 In accordance with the present invention there is further
09 provided a zeolite having a composition, as-synthesized and
10 in the anhydrous state, in terms of mole ratios as follows:

11

12 YO_2/W_2O_3 Greater than or equal to 15

13 YO_2/M_2O Greater than or equal to 45

14 YO_2/Q 10-40

15

16 wherein Q is comprised of cations selected from the group
17 consisting of N-benzyl-1,4-diazabicyclo[2.2.2]octane cations
18 and N-benzyl-1-azabicyclo[2.2.2]octane cations, M is an
19 alkali metal cation or alkaline earth metal cation, W is a
20 trivalent atom selected from the group consisting of boron,
21 aluminum, gallium, iron, titanium, and mixtures thereof
22 wherein at least 50% of W is boron, and Y is selected from
23 the group consisting of silicon, germanium, and mixtures
24 thereof and having the X-ray diffraction lines of Table I.

25

26 In accordance with this invention, there is also provided a
27 zeolite prepared by thermally treating (calcining) a zeolite
28 having a mole ratio of an oxide selected from silicon oxide,
29 germanium oxide and mixtures thereof to an oxide selected
30 from aluminum oxide, gallium oxide, iron oxide, titanium
31 oxide, boron oxide and mixtures thereof greater than about
32 10 and having the X-ray diffraction lines of Table I at a
33 temperature of from about 200°C (392°F) to about 800°C
34 (1472°F), the thus-treated zeolite having the X-ray

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01 diffraction lines of Table II. The present invention also
02 includes the hydrogen form of this thus-prepared zeolite,
03 which hydrogen form is prepared by ion exchanging with an
04 acid or with a solution of an ammonium salt followed by a
05 second thermal treatment.

06

07 In accordance with the present invention there is also
08 provided a catalyst comprising the aforesaid hydrogen form
09 of the zeolite of this invention.

10

11 The present invention additionally provides a process for
12 converting hydrocarbons comprising contacting a
13 hydrocarbonaceous feed at hydrocarbon converting conditions
14 with the catalyst of this invention.

15

16 Further provided by the present invention is a hydrocracking
17 process comprising contacting a hydrocarbon feedstock under
18 hydrocracking conditions with the catalyst of this
19 invention.

20

21 This invention also includes a dewaxing process comprising
22 contacting a hydrocarbon feedstock under dewaxing conditions
23 with the catalyst of this invention.

24

25 Also included in this invention is a process for increasing
26 the octane of a hydrocarbon feedstock to produce a product
27 having an increased aromatics content comprising contacting
28 a hydrocarbonaceous feedstock which comprises normal and
29 slightly branched hydrocarbons having a boiling range above
30 about 40°C (104°F) and less than about 300°C (572°F), under
31 aromatic conversion conditions with the zeolite of this
32 invention. Also provided in this invention is such a
33 process wherein the zeolite contains a Group VIII metal
34 component.

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01 Also provided by the present invention is a catalytic
02 cracking process comprising contacting a hydrocarbon
03 feedstock in a reaction zone under catalytic cracking
04 conditions in the absence of added hydrogen with a catalyst
05 comprising the aforementioned hydrogen form of the zeolite
06 of this invention.

07
08 Also included in this invention is such a catalytic cracking
09 process wherein the catalyst additionally comprises a large
10 pore crystalline cracking component.

11
12 The present invention further provides an isomerizing
13 process for isomerizing C₄ to C₇ hydrocarbons, comprising
14 contacting a catalyst, comprising at least one Group VIII
15 metal and the hydrogen form catalyst of this invention, with
16 a feed having normal and slightly branched C₄ to C₇
17 hydrocarbons under isomerizing conditions.

18
19 Also provided is such an isomerization process wherein the
20 catalyst has been calcined in a steam/air mixture at an
21 elevated temperature after impregnation of the Group VIII
22 metal, preferably platinum.

23
24 This invention also provides a process for alkylating an
25 aromatic hydrocarbon which comprises contacting under
26 alkylation conditions at least a molar excess of an aromatic
27 hydrocarbon with a C₂ to C₂₀ olefin under at least partial
28 liquid phase conditions and in the presence of the hydrogen
29 form catalyst of this invention.

30
31 This invention additionally provides a process for
32 transalkylating an aromatic hydrocarbon which comprises
33 contacting under transalkylating conditions an aromatic
34 hydrocarbon with a polyalkyl aromatic hydrocarbon under at

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01 least partial liquid phase conditions and in the presence of
02 the hydrogen form catalyst of this invention.

03

04 Further provided by this invention is a process to convert
05 paraffins to aromatics which comprises contacting paraffins
06 with the hydrogen form catalyst of this invention, said
07 catalyst comprising gallium, zinc, lead or indium or a
08 compound of gallium, zinc, lead or indium.

09

10 This invention also provides a process for converting lower
11 alcohols and other oxygenated hydrocarbons comprising
12 contacting said lower alcohol or other oxygenated
13 hydrocarbon with the hydrogen form catalyst of this
14 invention under conditions to produce liquid products.

15

16 This invention also provides a process for isomerizing
17 olefins comprising contacting said olefin with the catalyst
18 of this invention in its hydrogen form under conditions
19 which cause isomerization of the olefin. One example of
20 such a process is the isomerization of n-butene to
21 isobutene.

22

23 The full scope of the present invention will be apparent to
24 those familiar with molecular sieve synthesis from the
25 following detailed description of the principle features of
26 SSZ-42 and from the examples which accompany the
27 description.

28

29 BRIEF DESCRIPTION OF THE DRAWING

30

31 The drawing is a graph showing run hours versus temperature
32 for a reforming reaction using the catalyst of this
33 invention (plot A), a commercially available catalyst
34

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01 (plots B and B') and a platinum-containing cesium beta
02 zeolite catalyst (plots C and C').

03

04 DETAILED DESCRIPTION OF THE INVENTION

05

06 Principle Features

07

08 The present invention comprises a family of crystalline
09 multidimensional large pore zeolites, SSZ-42. As used
10 herein the term "large pore" means having an average pore
11 size diameter greater than about 6 Angstroms, preferably
12 from about 6.5 Angstroms to about 7.5 Angstroms.

13

14 SSZ-42 zeolites can be prepared from an aqueous solution
15 comprising sources of an alkali or alkaline earth metal
16 oxide, the templating agent, and sources of the desired
17 trivalent element oxides and tetravalent element oxides. The
18 reaction mixture should have a composition, in terms of mole
19 ratios, within the ranges shown in Table A.

20

21 TABLE A
22 SSZ-42 REACTION MIXTURE

		<u>Broad</u>	<u>Preferred</u>
24	YO ₂ /W ₂ O ₃	5 and greater (to about 100)	15 and greater (to about 100)
25	OH ⁻ /YO ₂	0.05 to 0.50	0.15 to 0.30
26	Q/YO ₂	0.10 to 1.0	0.10 to 0.25
27	M ⁺ /YO ₂	0.01 to 0.50	0.03 to 0.10
28	H ₂ O/YO ₂	15 to 100	20 to 50
29	Q/Q+M ⁺	0.50 to 0.95	0.66 to 0.90

30 wherein Q is comprised of cations selected from the group
31 consisting of N-benzyl-1,4-diazabicyclo[2.2.2]octane cations
32 and N-benzyl-1-azabicyclo[2.2.2]octane cations, M is an
33 alkali metal cation or alkaline earth metal cation, W is
34

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01 selected from the group aluminum, gallium, iron, boron,
02 titanium and mixtures thereof wherein at least 50% of W is
03 boron, and Y is selected from the group consisting of
04 silicon, germanium, and mixtures thereof.
05

06 SSZ-42 can be made essentially aluminum free, i.e., having a
07 silica to alumina mole ratio of ∞ . The term "essentially
08 alumina-free" is used because it is difficult to prepare
09 completely aluminum-free reaction mixtures for synthesizing
10 these materials. Especially when commercial silica sources
11 are used, aluminum is almost always present to a greater or
12 lesser degree. The hydrothermal reaction mixtures from
13 which the essentially alumina-free crystalline siliceous
14 molecular sieves may be prepared can be referred to as being
15 substantially alumina free. By this usage is meant that no
16 aluminum is intentionally added to the reaction mixture,
17 e.g., as an alumina or aluminate reagent, and that to the
18 extent aluminum is present, it occurs only as a contaminant
19 in the reagents. An additional method of increasing the
20 mole ratio of silica to alumina is by using standard acid
21 leaching or chelating treatments. However, essentially
22 aluminum-free SSZ-42 can be synthesized directly using
23 essentially aluminum-free silicon sources as the only
24 tetrahedral metal oxide component. SSZ-42 can also be
25 prepared directly as a borosilicate, or as an
26 alumino(boro)silicate by first preparing SSZ-42 as a
27 borosilicate and then substituting aluminum for at least a
28 portion of the boron by post synthesis treatment of the
29 borosilicate.
30

31 Lower silica to alumina ratios may also be obtained by using
32 methods which insert aluminum into the crystalline
33 framework. For example, aluminum insertion may occur by
34 thermal treatment of the zeolite in combination with an

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01 alumina binder or dissolved source of alumina. Such
02 procedures are described in U.S. Patent No. 4,559,315,
03 issued December 17, 1985 to Chang et al., which is
04 incorporated by reference herein in its entirety.

05
06 SSZ-42 as-synthesized has a mole ratio of tetravalent
07 element oxides selected from silicon oxide, germanium oxide,
08 and mixtures thereof to trivalent element oxides selected
09 from aluminum oxide, gallium oxide, iron oxide, boron oxide,
10 titanium oxide and mixtures thereof greater than about 10
11 wherein at least 50% of the trivalent element oxide is boron
12 oxide; and has the X-ray diffraction lines of Table I below.
13 SSZ-42 further has a composition, as-synthesized and in the
14 anhydrous state, in terms of mole ratios indicated in
15 Table B below.

TABLE B
AS-SYNTHESIZED SSZ-42

20 $\text{YO}_2/\text{W}_2\text{O}_3$ Greater than or equal to 15
21 $\text{YO}_2/\text{M}_2\text{O}$ Greater than or equal to 45
22 YO_2/Q 10-40

24 wherein Q, Y, W and M are as defined above, and wherein at
25 least 50% of W is boron.

27 It is believed that SSZ-42 is comprised of a new framework
28 structure or topology which is characterized by its X-ray
29 diffraction pattern. SSZ-42 zeolites, as-synthesized, have
30 a crystalline structure whose X-ray powder diffraction
31 pattern exhibit the characteristic lines shown in Table I
32 and is thereby distinguished from other known zeolites.

33
34

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01
 02 TABLE I
 03 AS-SYNTHESIZED SSZ-42

04	2Theta	d/n	100 I/I.
05	8.26	10.70	70
06	9.76	9.05	7
07	16.54	5.355	15
08	19.16	4.628	21
09	20.64	4.300	100
10	21.58	4.115	23
11	21.80	4.074	49
12	23.72	3.748	10
13	23.92	3.717	35
14	24.96	3.565	11
15	25.38	3.506	12
16	26.24	3.393	26
17	26.78	3.326	26
	29.46	3.030	18

18 The variation in the scattering angle (two theta)
 19 measurements, due to instrument error and to differences
 20 between individual samples, is estimated at +/- 0.20
 21 degrees.

22
 23 The X-ray diffraction pattern of Table I is representative
 24 of as-synthesized SSZ-42 zeolites. Minor variations in the
 25 diffraction pattern can result from variations in the
 26 silica-to-alumina or silica-to-boron mole ratio of the
 27 particular sample due to changes in lattice constants. In
 28 addition, sufficiently small crystals will affect the shape
 29 and intensity of peaks, leading to significant peak
 30 broadening.

31
 32
 33
 34

-13-

01 After calcination, the SSZ-42 zeolites have a crystalline
02 structure whose X-ray powder diffraction pattern include the
03 characteristic lines shown in Table II:

04

05

TABLE II
CALCINED SSZ-42

06

07	2Theta	d/n	100 I/I.
08	8.22	10.75	100
09	9.76	9.06	13
10	16.42	5.394	3
11	19.22	4.615	7
12	20.48	4.333	30
13	20.84	4.259	25
14	21.48	4.134	7
15	21.72	4.088	16
16	23.68	3.754	6
17	24.06	3.696	15
18	24.94	3.568	10
19	25.40	3.504	6
20	26.60	3.348	20
	29.56	3.019	10

21

22 The variation in the scattering angle (two theta)
23 measurements, due to instrument error and to indifferences
24 between individual samples, is estimated at +/- 0.20
25 degrees.

26

27 Representative peaks from the X-ray diffraction pattern of
28 calcined SSZ-42 are shown in Table II. Calcination can also
29 result in changes in the intensities of the peaks as
30 compared to patterns of the "as-synthesized" material, as
31 well as minor shifts in the diffraction pattern. The
32 zeolite produced by exchanging the metal or other cations
33 present in the zeolite with various other cations (such as
34 H⁺ or NH₄⁺) yields essentially the same diffraction pattern,

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01 although again, there may be minor shifts in the interplanar
02 spacing and variations in the relative intensities of the
03 peaks. Notwithstanding these minor perturbations, the basic
04 crystal lattice remains unchanged by these treatments.
05

06 The X-ray powder diffraction patterns were determined by
07 standard techniques. The radiation was the K-alpha/doublet
08 of copper. A scintillation counter spectrometer with a
09 strip-chart pen recorder was used. The peak heights I and
10 the positions, as a function of 2θ where θ is the Bragg
11 angle, were read from the relative intensities, I/I_0 , where I_0
12 is the intensity of the strongest line or peak, and d , the
13 interplanar spacing in Angstroms corresponding to the
14 recorded lines, can be calculated.
15

16 The Preparation of SSZ-42 Zeolites
17

18 In preparing SSZ-42 zeolites, an N-benzyl-1,4-
19 diazabicyclo[2.2.2]octane cation or N-benzyl-1-aza-
20 bicyclo[2.2.2]octane cation may be used as a crystallization
21 template in a manner known in the molecular sieve art.
22 Thus, in general, SSZ-42 is prepared by contacting an active
23 source of one or more oxides selected from the group
24 consisting of monovalent element oxides, divalent element
25 oxides, trivalent element oxides, and tetravalent element
26 oxides with an organocation templating agent.
27

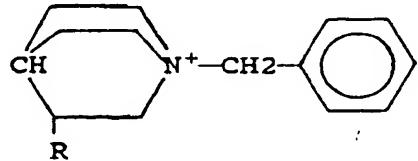
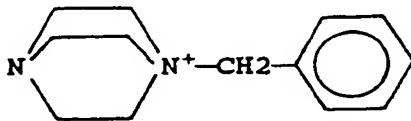
28 In practice, SSZ-42 is prepared by a process comprising:
29

30 (a) preparing an aqueous solution containing sources
31 of the oxides listed in Table A above and at least one
32 N-benzyl-1,4-diazabicyclo[2.2.2]octane cation or N-
33 benzyl-1-azabicyclo[2.2.2]octane cation templating
34

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01 agent having an anionic counterion which is not
02 detrimental to the formation of SSZ-42;
03
04 (b) maintaining the aqueous solution under conditions
05 sufficient to form crystals of SSZ-42; and
06
07 (c) recovering the crystals of SSZ-42.

09 The N-benzyl-1,4-diazabicyclo[2.2.2]octane cation and N-
10 benzyl-1-azabicyclo[2.2.2]octane cation templating agents
11 which have been found to produce SSZ-42 have the following
12 general formulas:



18 where R is -H, -OH or -NH₂.

20 Examples of the N-benzyl-1,4-diazabicyclo[2.2.2]octane
21 cation templating agents useful in this invention include,
22 but are not limited to, N-benzyl-1,4-
23 diazabicyclo[2.2.2]octane cation, and examples of the
24 N-benzyl-1-azabicyclo[2.2.2]octane cation templating agents
25 useful in this invention include, but are not limited to,
26 N-benzyl-1-azabicyclo[2.2.2]octane cation and N-benzyl-3-
27 hydroxy-1-azabicyclo[2.2.2]octane cation.

29 SSZ-42 may comprise the crystalline material and the
30 templating agent in combination with metallic and
31 non-metallic oxides bonded in tetrahedral coordination
32 through shared oxygen atoms to form a cross-linked three
33 dimensional crystal structure. The metallic and
34

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1 non-metallic oxides comprise one or a combination of oxides
2 selected from the group consisting of one or more trivalent
3 element(s), and one or more tetravalent element(s). The
4 trivalent element is preferably selected from the group
5 consisting of aluminum, boron, gallium, iron, titanium with
6 at least 50% of the trivalent element being boron. Once the
7 as-synthesized SSZ-42 material has been made, some or all of
8 the boron may be replaced with, e.g., aluminum. Thus, in
9 the calcined version of SSZ-42, the trivalent element is
10 preferably aluminum, boron or combinations thereof. The
11 tetravalent element is preferably selected from the group
12 consisting of silicon, germanium, and combinations thereof.
13 More preferably, the tetravalent element is silicon.
14
15 Typical sources of silicon oxide include silicates, silica
16 hydrogel, silicic acid, fumed silica, colloidal silica,
17 tetra-alkyl orthosilicates, and silica hydroxides. Boron,
18 as well as gallium, germanium, titanium, and iron can be
19 added in forms corresponding to their silicon counterparts,
20 i.e., as borates, boric acid and the like.
21
22 Typical sources of aluminum oxide for the reaction mixture
23 include aluminates, alumina and aluminum compounds such as
24 AlCl_3 , $\text{Al}(\text{SO}_4)_3$, hydrated $\text{Al}(\text{OH})_3$, gels, kaolin clays,
25 colloidal aluminas, and the like.
26
27 Alternatively, a zeolite reagent may provide a source of
28 aluminum or boron. In some cases, the source zeolite may
29 provide a source of silica. In that case, the source
30 zeolite in its dealuminated or deboronated form may be used
31 as a source of silica, with additional silicon added using,
32 for example, the conventional sources listed above. Use of
33 a source zeolite reagent as a source of alumina for the
34 present process is described in U.S. Patent No. 4,503,024

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01 issued on March 5, 1985 to Bourgogne, et al. entitled
02 "PROCESS FOR THE PREPARATION OF SYNTHETIC ZEOLITES, AND
03 ZEOLITES OBTAINED BY SAID PROCESS", the disclosure of which
04 is incorporated herein by reference.

05

06 Typically, an alkali metal hydroxide and/or an alkaline
07 earth metal hydroxide, such as the hydroxide of sodium,
08 potassium, lithium, cesium, rubidium, calcium, and
09 magnesium, is used in the reaction mixture; however, this
10 component can be omitted so long as the equivalent basicity
11 is maintained. The templating agent may be used to provide
12 hydroxide ion. Thus, it may be beneficial to ion exchange,
13 for example, a hydroxide anion for a halide ion in the
14 templating agent, thereby reducing or eliminating the alkali
15 or alkaline earth metal hydroxide quantity required. The
16 alkali metal cation or alkaline earth cation may be part of
17 the as-synthesized crystalline oxide material, in order to
18 balance valence electron charges therein.

19

20 The reaction mixture is maintained at an elevated
21 temperature until the crystals of the SSZ-42 zeolite are
22 formed. This hydrothermal crystallization is usually
23 conducted under autogenous pressure, at a temperature
24 between 100°C (212°F) and 200°C (392°F), preferably between
25 135° (275°F) and 180°C (356°F). The crystallization period
26 is typically greater than 1 day and preferably from about 3
27 days to about 7 days. The zeolite can be prepared with or
28 without mild stirring or agitation.

29

30 During the hydrothermal crystallization step, the SSZ-42
31 crystals can be allowed to nucleate spontaneously from the
32 reaction mixture. However, the use of SSZ-42 crystals as
33 seed material can be advantageous in decreasing the time
34 necessary for complete crystallization to occur. In

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01 addition, seeding can lead to an increased purity of the
02 product obtained by promoting the nucleation and/or
03 formation of SSZ-42 over any undesired phases. When used as
04 seeds, SSZ-42 crystals are added in an amount between 0.1
05 and 10% of the weight of silica used in the reaction
06 mixture.

07

08 Once the zeolite crystals have formed, the solid product is
09 separated from the reaction mixture by standard mechanical
10 separation techniques such as filtration. The crystals are
11 water-washed and then dried, e.g., at 90°C (194°F) to 150°C
12 (302°F) for from 8 to 24 hours, to obtain the
13 as-synthesized, SSZ-42 zeolite crystals. The drying step
14 can be performed at atmospheric pressure or under vacuum.

15

16 Crystalline SSZ-42 can be used as-synthesized or can be
17 thermally treated (calcined). Usually, it is desirable to
18 remove the alkali or alkaline earth metal cation by ion
19 exchange and replace it with hydrogen, ammonium, or any
20 desired metal ion. The zeolite can be leached with
21 chelating agents, e.g., EDTA or dilute acid solutions, to
22 increase the silica to alumina mole ratio. The zeolite can
23 also be steamed; steaming helps stabilize the crystalline
24 lattice to attack from acids. The zeolite can be used in
25 intimate combination with hydrogenating components, such as
26 tungsten, vanadium, molybdenum, rhenium, nickel, cobalt,
27 chromium, manganese, or a noble metal, such as palladium or
28 platinum, for those applications in which a
29 hydrogenation-dehydrogenation function is desired.

30

31 Metals may also be introduced into the zeolite by replacing
32 some of the cations in the zeolite with metal cations via
33 ion exchange techniques. Typical replacing cations can
34 include metal cations, e.g., rare earth, Group IIA and Group

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01 VIII metals, as well as their mixtures. Of the replacing
02 metallic cations, cations of metals such as rare earth, Mn,
03 Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, and Fe are
04 particularly preferred.

05

06 The hydrogen, ammonium, and metal components can be
07 ion-exchanged into the SSZ-42. The zeolite can also be
08 impregnated with the metals, or the metals can be physically
09 and intimately admixed with the zeolite using standard
10 methods known to the art.

11

12 Typical ion-exchange techniques involve contacting the
13 synthetic zeolite with a solution containing a salt of the
14 desired replacing cation or cations. Although a wide
15 variety of salts can be employed, chlorides and other
16 halides, acetates, nitrates, and sulfates are particularly
17 preferred. The zeolite is usually calcined prior to the
18 ion-exchange procedure to remove the organic matter present
19 in the channels and on the surface, since this results in a
20 more effective ion exchange. Representative ion exchange
21 techniques are disclosed in a wide variety of patents
22 including U.S. Patent Nos. 3,140,249 issued on July 7, 1964
23 to Plank, et al.; 3,140,251 issued on July 7, 1964 to
24 Plank, et al.; and 3,140,253 issued on July 7, 1964 to
25 Plank, et al., each of which is incorporated by reference
26 herein.

27

28 Following contact with the salt solution of the desired
29 replacing cation, the zeolite is typically washed with water
30 and dried at temperatures ranging from 65°C (149°F) to about
31 200°C (392°F). After washing, the zeolite can be calcined
32 in air or inert gas at temperatures ranging from about 200°C
33 (392°F) to about 800°C (1472°F) for periods of time ranging
34 from 1 to 48 hours, or more, to produce a catalytically

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01 active product especially useful in hydrocarbon conversion
02 processes.
03
04 Regardless of the cations present in the synthesized form of
05 SSZ-42, the spatial arrangement of the atoms which form the
06 basic crystal lattice of the zeolite remains essentially
07 unchanged. The exchange of cations has little, if any
08 effect on the zeolite lattice structure.
09
10 SSZ-42 can be formed into a wide variety of physical shapes.
11 Generally speaking, the zeolite can be in the form of a
12 powder, a granule, or a molded product, such as extrudate
13 having a particle size sufficient to pass through a 2-mesh
14 (Tyler) screen and be retained on a 400-mesh (Tyler) screen.
15 In cases where the catalyst is molded, such as by extrusion
16 with an organic binder, the zeolite can be extruded before
17 drying, or, dried or partially dried and then extruded.
18
19 SSZ-42 can be composited with other materials resistant to
20 the temperatures and other conditions employed in organic
21 conversion processes. Such matrix materials include active
22 and inactive materials and synthetic or naturally occurring
23 zeolites as well as inorganic materials such as clays,
24 silica and metal oxides. Examples of such materials and the
25 manner in which they can be used are disclosed in United
26 States Patent No. 4,910,006, issued May 20, 1990 to Zones
27 et al., and copending U.S. Patent Application No. 959,205,
28 filed October 9, 1992 entitled "ZEOLITE SSZ-35", both of
29 which are incorporated by reference herein in their
30 entirety.
31
32
33
34

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Hydrocarbon Conversion Processes

02

03 SSZ-42 zeolites are useful in hydrocarbon conversion
04 reactions. Hydrocarbon conversion reactions are chemical
05 and catalytic processes in which carbon containing compounds
06 are changed to different carbon containing compounds.
07 Examples of hydrocarbon conversion reactions in which SSZ-42
08 are expected to be useful include catalytic cracking,
09 hydrocracking, dewaxing, alkylation, and olefin and
10 aromatics formation reactions. The catalysts are also
11 expected to be useful in other petroleum refining and
12 hydrocarbon conversion reactions such as isomerizing
13 n-paraffins and naphthenes, polymerizing and oligomerizing
14 olefinic or acetylenic compounds such as isobutylene and
15 butene-1, reforming, alkylating, isomerizing polyalkyl
16 substituted aromatics. (e.g., m-xylene), and
17 disproportionating aromatics (e.g., toluene) to provide
18 mixtures of benzene, xylenes and higher methylbenzenes and
19 oxidation reactions. The SSZ-42 catalysts have high
20 selectivity, and under hydrocarbon conversion conditions can
21 provide a high percentage of desired products relative to
22 total products.

23

24 SSZ-42 zeolites can be used in processing hydrocarbonaceous
25 feedstocks. Hydrocarbonaceous feedstocks contain carbon
26 compounds and can be from many different sources, such as
27 virgin petroleum fractions, recycle petroleum fractions,
28 shale oil, liquefied coal, tar sand oil, and, in general,
29 can be any carbon containing fluid susceptible to zeolitic
30 catalytic reactions. Depending on the type of processing
31 the hydrocarbonaceous feed is to undergo, the feed can
32 contain metal or be free of metals, it can also have high or
33 low nitrogen or sulfur impurities. It can be appreciated,
34 however, that in general processing will be more efficient

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01 (and the catalyst more active) the lower the metal,
02 nitrogen, and sulfur content of the feedstock.
03
04 The conversion of hydrocarbonaceous feeds can take place in
05 any convenient mode, for example, in fluidized bed, moving
06 bed, or fixed bed reactors depending on the types of process
07 desired. The formulation of the catalyst particles will
08 vary depending on the conversion process and method of
09 operation.
10
11 Other reactions which can be performed using the catalyst of
12 this invention containing a metal, e.g., a Group VIII metal
13 such platinum, include hydrogenation-dehydrogenation
14 reactions, denitrogenation and desulfurization reactions.
15
16 SSZ-42 can be used in hydrocarbon conversion reactions with
17 active or inactive supports, with organic or inorganic
18 binders, and with and without added metals. These reactions
19 are well known to the art, as are the reaction conditions.
20

21 Hydrocracking
22

23 Using SSZ-42 catalyst which contains a hydrogenation
24 promoter, heavy petroleum residual feedstocks, cyclic stocks
25 and other hydrocrackate charge stocks can be hydrocracked
26 using the process conditions and catalyst components
27 disclosed in the aforementioned U.S. Patent No. 4,910,006
28 and U.S. Patent Application No. 959,205. Typically, these
29 feedstocks can be hydrocracked at hydrocracking conditions
30 including a temperature in the range of from 175°C (347°F)
31 to 485°C (905°F), molar ratios of hydrogen to hydrocarbon
32 charge from 1 to 100, a pressure in the range of from 0.5 to
33 350 bar, and a liquid hourly space velocity (LHSV) in the
34 range of from 0.1 to 30.

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01 The hydrocracking catalysts contain an effective amount of
02 at least one hydrogenation component of the type commonly
03 employed in hydrocracking catalysts. The hydrogenation
04 component is generally selected from the group of
05 hydrogenation catalysts consisting of one or more metals of
06 Group VIB and Group VIII, including the salts, complexes and
07 solutions containing such. The hydrogenation catalyst is
08 preferably selected from the group of metals, salts and
09 complexes thereof of the group consisting of at least one of
10 platinum, palladium, rhodium, iridium and mixtures thereof
11 or the group consisting of at least one of nickel,
12 molybdenum, cobalt, tungsten, titanium, chromium and
13 mixtures thereof. Reference to the catalytically active
14 metal or metals is intended to encompass such metal or
15 metals in the elemental state or in some form such as an
16 oxide, sulfide, halide, carboxylate and the like.
17
18 The hydrogenation catalyst is present in an effective amount
19 to provide the hydrogenation function of the hydrocracking
20 catalyst, and preferably in the range of from 0.05 to 25% by
21 weight.

22

Dewaxing

24

25 SSZ-42 can be used to dewax hydrocarbonaceous feeds by
26 selectively removing straight chain paraffins. The
27 catalytic dewaxing conditions are dependent in large measure
28 on the feed used and upon the desired pour point.
29 Generally, the temperature will be between about 200°C
30 (392°F) and about 475°C (887°F), preferably between about
31 250°C (482°F) and about 450°C (842°F). The pressure is
32 typically between about 15 psig and about 3000 psig,
33 preferably between about 200 psig and 3000 psig. The liquid
34

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01 hourly space velocity (LHSV) preferably will be from 0.1 to
02 20, preferably between about 0.2 and about 10.

03

04 Hydrogen is preferably present in the reaction zone during
05 the catalytic dewaxing process. The hydrogen to feed ratio
06 is typically between about 500 and about 30,000 SCF/bbl
07 (standard cubic feet per barrel), preferably about 1000 to
08 about 20,000 SCF/bbl. Generally, hydrogen will be separated
09 from the product and recycled to the reaction zone. Typical
10 feedstocks include light gas oil, heavy gas oils and reduced
11 crudes boiling about 177°C (350°F).

12

13 The SSZ-42 hydrodewaxing catalyst may optionally contain a
14 hydrogenation component of the type commonly employed in
15 dewaxing catalysts. See the aforementioned U.S. Patent
16 No. 4,910,006 and U.S. Patent Application No. 959,205 for
17 examples of these hydrogenation components. The
18 hydrogenation component is present in an effective amount to
19 provide an effective hydrodewaxing and hydroisomerization
20 catalyst preferably in the range of from about 0.05 to 5% by
21 weight. The catalyst may be run in such a mode to increase
22 isodewaxing at the expense of cracking reactions.

23

24 Aromatics Formation

25

26 SSZ-42 can be used to convert light straight run naphthas
27 and similar mixtures to highly aromatic mixtures. Thus,
28 normal and slightly branched chained hydrocarbons,
29 preferably having a boiling range above about 40°C (104°F)
30 and less than about 300°C (572°F), can be converted to
31 products having a substantial higher octane aromatics
32 content by contacting the hydrocarbon feed with the zeolite
33 at a temperature in the range of from about 400°C (752°F) to
34 600°C (1112°F), preferably 480°C (896°F) to 550°C (1022°F)

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01 at pressures ranging from atmospheric to 10 bar, and liquid
02 hourly space velocities (LHSV) ranging from 0.1 to 15.

03

04 The conversion catalyst preferably contains a Group VIII
05 metal compound to have sufficient activity for commercial
06 use. By Group VIII metal compound as used herein is meant
07 the metal itself or a compound thereof. The Group VIII
08 noble metals and their compounds, platinum, palladium, and
09 iridium, or combinations thereof can be used. Rhenium or
10 tin or a mixture thereof may also be used in conjunction
11 with the Group VIII metal compound and preferably a noble
12 metal compound. The most preferred metal is platinum. The
13 amount of Group VIII metal present in the conversion
14 catalyst should be within the normal range of use in
15 reforming catalysts, from about 0.05 to 2.0 weight percent,
16 preferably 0.2 to 0.8 weight percent.

17

18 It is critical to the selective production of aromatics in
19 useful quantities that the conversion catalyst be
20 substantially free of acidity, for example, by neutralizing
21 the zeolite with a basic metal, e.g., alkali metal,
22 compound. Methods for rendering the catalyst free of
23 acidity are known in the art. See the aforementioned U.S.
24 Patent No. 4,910,006 and U.S. Patent Application No. 959,205
25 for a description of such methods.

26

27 The preferred alkali metals are sodium, potassium, and
28 cesium. The zeolite itself can be substantially free of
29 acidity only at very high silica:alumina mole ratios; by
30 "zeolite consisting essentially of silica" is meant a
31 zeolite which is substantially free of acidity without base
32 neutralization.

33

34

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01

Catalytic Cracking

02

03 Hydrocarbon cracking stocks can be catalytically cracked in
04 the absence of hydrogen using SSZ-42 at liquid hourly space
05 velocities from 0.5 to 50, temperatures from about 127°C
06 (260°F) to 885°C (1625°F) and pressures from subatmospheric
07 to several hundred atmospheres, typically from about
08 atmospheric to about 5 atmospheres.

09

10 For this purpose, the SSZ-42 catalyst can be composited with
11 mixtures of inorganic oxide supports as well as a
12 traditional large pore crystalline cracking catalyst.

13

14 As in the case of hydrocracking catalysts, when SSZ-42 is
15 used as a catalytic cracking catalyst in the absence of
16 hydrogen, the catalyst may be employed in conjunction with
17 traditional cracking catalysts, e.g., any aluminosilicate
18 heretofore employed as a component in cracking catalysts.
19 Examples of these traditional cracking catalysts are
20 disclosed in the aforementioned U.S. Patent No. 4,910,006
21 and U.S. Patent Application No. 959,205. When a traditional
22 cracking catalyst (TC) component is employed, the relative
23 weight ratio of the TC to the SSZ-42 is generally between
24 about 1:10 and about 500:1, desirably between about 1:10 and
25 about 200:1, preferably between about 1:2 and about 50:1,
26 and most preferably is between about 1:1 and about 20:1.

27

28 The cracking catalysts are typically employed with an
29 inorganic oxide matrix component. See the aforementioned
30 U.S. Patent No. 4,910,006 and U.S. Patent Application
31 No. 959,205 for examples of such matrix components.

32

33

34

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Oligomerization

01
02
03 It is expected that SSZ-42 can also be used to oligomerize
04 straight and branched chain olefins having from about 2 to
05 21 and preferably 2-5 carbon atoms. The oligomers which are
06 the products of the process are medium to heavy olefins
07 which are useful for both fuels, i.e., gasoline or a
08 gasoline blending stock and chemicals.
09
10 The oligomerization process comprises contacting the olefin
11 feedstock in the gaseous state phase with SSZ-42 at a
12 temperature of from about 232°C (450°F) to about 649°C
13 (1200°F), a LHSV of from about 0.2 to about 50 and a
14 hydrocarbon partial pressure of from about 0.1 to about 50
15 atmospheres.
16
17 Also, temperatures below about 232°C (450°F) may be used to
18 oligomerize the feedstock, when the feedstock is in the
19 liquid phase when contacting the zeolite catalyst. Thus,
20 when the olefin feedstock contacts the zeolite catalyst in
21 the liquid phase, temperatures of from about 10°C (50°F) to
22 about 232°C (450°F), and preferably from 27°C (80°F) to
23 204°C (400°F) may be used and a WHSV of from about 0.05 to
24 20 and preferably 0.1 to 10. It will be appreciated that
25 the pressures employed must be sufficient to maintain the
26 system in the liquid phase. As is known in the art, the
27 pressure will be a function of the number of carbon atoms of
28 the feed olefin and the temperature. Suitable pressures
29 include from about 0 psig to about 3000 psig.
30
31 The zeolite can have the original cations associated
32 therewith replaced by a wide variety of other cations
33 according to techniques well known in the art. Typical
34 cations would include hydrogen, ammonium and metal cations

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01 including mixtures of the same. Of the replacing metallic
02 cations, particular preference is given to cations of metals
03 such as rare earth metals, manganese, calcium, as well as
04 metals of Group II of the Periodic Table, e.g., zinc, and
05 Group VIII of the Periodic Table, e.g., nickel. One of the
06 prime requisites is that the zeolite have a fairly low
07 aromatization activity, i.e., in which the amount of
08 aromatics produced is not more than about 20% by weight.
09 This is accomplished by using a zeolite with controlled acid
10 activity [alpha value] of from about 0.1 to about 120,
11 preferably from about 0.1 to about 100, as measured by its
12 ability to crack n-hexane.

13

14 Alpha values are defined by a standard test known in the
15 art, e.g., as shown in U.S. Patent No. 3,960,978 issued on
16 June 1, 1976 to Givens, et al. which is incorporated totally
17 herein by reference. If required, such zeolites may be
18 obtained by steaming, by use in a conversion process or by
19 any other method which may occur to one skilled in this art.
20

21 SSZ-42 can be used to convert light gas C₂-C₆ paraffins
22 and/or olefins to higher molecular weight hydrocarbons
23 including aromatic compounds. Operating temperatures of
24 100°C (212°F) to 700°C (1292°F), operating pressures of 0 to
25 1000 psig and space velocities of 0.5-40 hr⁻¹ WHSV (weight
26 hourly space velocity) can be used to convert the C₂-C₆
27 paraffin and/or olefins to aromatic compounds. Preferably,
28 the zeolite will contain a catalyst metal or metal oxide
29 wherein said metal is selected from the group consisting of
30 Groups IB, IIB, VIII and IIIA of the Periodic Table, and
31 most preferably gallium or zinc and in the range of from
32 about 0.05% to 5% by weight.

33

34

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Condensation of Alcohols

02
03 SSZ-42 can be used to condense lower aliphatic alcohols
04 having 1 to 10 carbon atoms to a gasoline boiling point
05 hydrocarbon product comprising mixed aliphatic and aromatic
06 hydrocarbon. The condensation reaction proceeds at a
07 temperature of about 260°C (500°F) to 538°C (1000°F), a
08 pressure of about 0.5 psig to 1000 psig and a space velocity
09 of about 0.5 to 50 WHSV. The process disclosed in U.S.
10 Patent No. 3,894,107 issued July 8, 1975 to Butter et al.,
11 describes the process conditions used in this process, which
12 patent is incorporated totally herein by reference.

13
14 The catalyst may be in the hydrogen form or may be base
15 exchanged or impregnated to contain ammonium or a metal
16 cation complement, preferably in the range of from about
17 0.05 to 5% by weight. The metal cations that may be present
18 include any of the metals of the Groups I through VIII of
19 the Periodic Table. However, in the case of Group IA
20 metals, the cation content should in no case be so large as
21 to effectively inactivate the catalyst.

Isomerization

25 The present catalyst is highly active and highly selective
26 for isomerizing C₄ to C₅ hydrocarbons. The activity means
27 that the catalyst can operate at relatively low temperature
28 which thermodynamically favors highly branched paraffins.
29 Consequently, the catalyst can produce a high octane
30 product. The high selectivity means that a relatively high
31 liquid yield can be achieved when the catalyst is run at a
32 high octane.

33

34

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01 The present process comprises contacting the isomerization
02 catalyst with a hydrocarbon feed under isomerization
03 conditions. The feed is preferably a light straight run
04 fraction, boiling within the range of -1.1°C (30°F) to 121°C
05 (250°F) and preferably from 16°C (60°F) to 93°C (200°F).
06 Preferably, the hydrocarbon feed for the process comprises a
07 substantial amount of C₄ to C₇ normal and slightly branched
08 low octane hydrocarbons, more preferably C₅ and C₆
09 hydrocarbons.
10
11 The pressure in the process is preferably between 50 psig
12 and 1000 psig, more preferably between 100 psig and
13 500 psig. The liquid hourly space velocity (LHSV) is
14 preferably between about 1 to about 10 with a value in the
15 range of about 1 to about 4 being more preferred. It is
16 also preferable to carry out the isomerization reaction in
17 the presence of hydrogen. Preferably, hydrogen is added to
18 give a hydrogen to hydrocarbon ratio (H₂/HC) of between 0.5
19 and 10 H₂/HC, more preferably between 1 and 8 H₂/HC. The
20 temperature is preferably between about 93°C (200°F) and
21 about 538°C (1000°F), more preferably between 204°C (400°F)
22 and 316°C (600°F). See the aforementioned U.S. Patent
23 No. 4,910,006 and U.S. Patent Application No. 959,205 for a
24 further discussion of isomerization process conditions.
25
26 A low sulfur feed is especially preferred in the present
27 process. The feed preferably contains less than 10 ppm,
28 more preferably less than 1 ppm, and most preferably less
29 than 0.1 ppm sulfur. In the case of a feed which is not
30 already low in sulfur, acceptable levels can be reached by
31 hydrogenating the feed in a presaturation zone with a
32 hydrogenating catalyst which is resistant to sulfur
33 poisoning. See the aforementioned U.S. Patent No. 4,910,006
34

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01 and U.S. Patent Application No. 959,205 for a further
02 discussion of this hydrodesulfurization process.

03

04 It is preferable to limit the nitrogen level and the water
05 content of the feed. Catalysts and processes which are
06 suitable for these purposes are known to those skilled in
07 the art.

08

09 After a period of operation, the catalyst can become
10 deactivated by sulfur or coke. See the aforementioned U.S.
11 Patent No. 4,910,006 and U.S. Patent Application No. 959,205
12 for a further discussion of methods of removing this sulfur
13 and coke, and of regenerating the catalyst.

14

15 The conversion catalyst preferably contains a Group VIII
16 metal compound to have sufficient activity for commercial
17 use. By Group VIII metal compound as used herein is meant
18 the metal itself or a compound thereof. The Group VIII
19 noble metals and their compounds, platinum, palladium, and
20 iridium, or combinations thereof can be used. Rhenium and
21 tin may also be used in conjunction with the noble metal.
22 The most preferred metal is platinum. The amount of
23 Group VIII metal present in the conversion catalyst should
24 be within the normal range of use in isomerizing catalysts,
25 from about 0.05 to 2.0 weight percent, preferably 0.2 to
26 0.8 weight percent.

27

28 The isomerization catalyst may also be calcined in a
29 steam/air mixture at an elevated temperature after
30 impregnation with the Group VIII metal, preferably platinum.

31

32

33

34

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01

Alkylation and Transalkylation

02

03 SSZ-42 can be used in a process for the alkylation or
04 transalkylation of an aromatic hydrocarbon. The process
05 comprises contacting the aromatic hydrocarbon with a C₂ to
06 C₁₆ olefin alkylating agent or a polyalkyl aromatic
07 hydrocarbon transalkylating agent, under at least partial
08 liquid phase conditions, and in the presence of a catalyst
09 comprising SSZ-42.

10

11 SSZ-42 can also be used for removing benzene from gasoline
12 by alkylating the benzene as described above and removing
13 the alkylated product from the gasoline.

14

15 For high catalytic activity, the SSZ-42 zeolite should be
16 predominantly in its hydrogen ion form. Generally, the
17 zeolite is converted to its hydrogen form by ammonium
18 exchange followed by calcination. If the zeolite is
19 synthesized with a high enough ratio of organo-nitrogen
20 cation to sodium ion, calcination alone may be sufficient.
21 It is preferred that, after calcination, at least 80% of the
22 cation sites are occupied by hydrogen ions and/or rare earth
23 ions.

24

25 The pure SSZ-42 zeolite may be used as a catalyst, but
26 generally it is preferred to mix the zeolite powder with an
27 inorganic oxide binder such as alumina, silica,
28 silica/alumina, or naturally occurring clays and form the
29 mixture into tablets or extrudates. The final catalyst may
30 contain from 1 to 99 weight percent SSZ-42 zeolite. Usually
31 the zeolite content will range from 10 to 90 weight percent,
32 and more typically from 60 to 80 weight percent. The
33 preferred inorganic binder is alumina. The mixture may be
34

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01 formed into tablets or extrudates having the desired shape
02 by methods well known in the art.

03

04 Examples of suitable aromatic hydrocarbon feedstocks which
05 may be alkylated or transalkylated by the process of the
06 invention include aromatic compounds such as benzene,
07 toluene and xylene. The preferred aromatic hydrocarbon is
08 benzene. Mixtures of aromatic hydrocarbons may also be
09 employed.

10

11 Suitable olefins for the alkylation of the aromatic
12 hydrocarbon are those containing 2 to 20, preferably 2 to
13 4, carbon atoms, such as ethylene, propylene, butene-1,
14 trans-butene-2 and cis-butene-2, or mixtures thereof. The
15 preferred olefin is propylene. These olefins may be present
16 in admixture with the corresponding C₂ to C₂₀ paraffins, but
17 it is preferable to remove any dienes, acetylenes, sulfur
18 compounds or nitrogen compounds which may be present in the
19 olefin feedstock stream, to prevent rapid catalyst
20 deactivation. Longer chain alpha olefins may be used as
21 well.

22

23 When transalkylation is desired, the transalkylating agent
24 is a polyalkyl aromatic hydrocarbon containing two or more
25 alkyl groups that each may have from 2 to about 4 carbon
26 atoms. For example, suitable polyalkyl aromatic
27 hydrocarbons include di-, tri- and tetra-alkyl aromatic
28 hydrocarbons, such as diethylbenzene, triethylbenzene,
29 diethylmethylbenzene (diethyltoluene), di-isopropylbenzene,
30 di-isopropyltoluene, dibutylbenzene, and the like.

31 Preferred polyalkyl aromatic hydrocarbons are the dialkyl
32 benzenes. A particularly preferred polyalkyl aromatic
33 hydrocarbon is di-isopropylbenzene.

34

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01 When alkylation is the process conducted, reaction
02 conditions are as follows. The aromatic hydrocarbon feed
03 should be present in stoichiometric excess. It is preferred
04 that molar ratio of aromatics to olefins be greater than
05 four-to-one to prevent rapid catalyst fouling. The reaction
06 temperature may range from 38°C (100°F) to 316°C (600°F),
07 preferably 121° (250°F) to 232° (450°F). The reaction
08 pressure should be sufficient to maintain at least a partial
09 liquid phase in order to retard catalyst fouling. This is
10 typically 50 psig to 1000 psig depending on the feedstock
11 and reaction temperature. Contact time may range from
12 10 seconds to 10 hours, but is usually from 5 minutes to an
13 hour. The weight hourly space velocity (WHSV), in terms of
14 grams (pounds) of aromatic hydrocarbon and olefin per gram
15 (pound) of catalyst per hour, is generally within the range
16 of about 0.5 to 50.
17
18 When transalkylation is the process conducted, the molar
19 ratio of aromatic hydrocarbon will generally range from
20 about 1:1 to 25:1, and preferably from about 2:1 to 20:1.
21 The reaction temperature may range from about 38°C (100°F)
22 to 316°C (600°F), but it is preferably about 121°C (250°F)
23 to 232°C (450°F). The reaction pressure should be
24 sufficient to maintain at least a partial liquid phase,
25 typically in the range of about 50 psig to 1000 psig,
26 preferably 300 psig to 600 psig. The weight hourly space
27 velocity will range from about 0.1 to 10. U.S. Patent
28 No. 5,082,990 issued on January 21, 1992 to Hsieh, et al.
29 describes such processes and is incorporated herein by
30 reference.
31
32 SSZ-42 can also be used as an adsorbent with high
33 selectivities based on molecular sieve behavior and also
34

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01 based upon preferential hydrocarbon packing within the
02 pores.

03

04 Xylene Isomerization

05

06 SSZ-42 may also be useful in a process for isomerizing one
07 or more xylene isomers in a C₈ aromatic feed to obtain
08 ortho-, meta- and para-xylene in a ratio approaching the
09 equilibrium value. In particular, xylene isomerization is
10 used in conjunction with a separation process to manufacture
11 para-xylene. For example, a portion of the para-xylene in a
12 mixed C₈ aromatics stream may be recovered by
13 crystallization and centrifugation. The mother liquor from
14 the crystallizer is then reacted under xylene isomerization
15 conditions to restore ortho-, meta- and para-xlenes to a
16 near equilibrium ratio. At the same time, part of the
17 ethylbenzene in the mother liquor is converted to xylenes or
18 to products which are easily separated by distillation. The
19 isomerate is blended with fresh feed and the combined stream
20 is distilled to remove heavy and light by-products. The
21 resultant C₈ aromatics stream is then sent to the
22 crystallizer to repeat the cycle.

23

24 EXAMPLES

25

26 The following examples demonstrate but do not limit the
27 present invention.

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03 Example 1
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05 Synthesis of N-benzyl-1,4-diazabicyclo[2.2.2]octane cation
06
07 145 Grams of 1,4-diazabicyclo[2.2.2]octane (commonly
08 referred to as "DABCO") was dissolved in 2.5 liters of ethyl
09 acetate and chilled to 0°C (32°F). 209 Grams of benzyl
10 bromide was added dropwise while the chilled solution was
11 stirred. Caution should be exercised because the reaction
12 is rapid and requires cooling. The product was collected by
13 filtration and recrystallized from a minimum of warm
14 methanol. The recrystallized product gave a microanalysis
15 and NMR pattern consistent with the 1:1 adduct. The
16 quaternary ammonium compound was ion exchanged using
17 hydroxide exchange resin AG1-X8 from BioRad. The exchanged
18 solution was titrated for molarity and the yield of exchange
Template A.

19
20 Example 2

SYNTHESIS OF 1-AZABICYCLO[2.2.2]OCTANE CATION

24 The procedure of Example 1 was repeated using the same molar
25 quantity of 1-azabicyclo[2.2.2]octane (commonly referred to
26 as "quinuclidine") as the DABCO in Example 1. This compound
27 was designated Template B.

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Example 3

02

03 The procedure of Example 1 was repeated using the same molar
04 quantity of 3-hydroxy-1-azabicyclo[2.2.2]octane in place of
05 the DABCO. The resulting compound was designated
06 Template C.

07

08

Example 4

09

Synthesis of SSZ-42

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11 3 Millimoles of Template A as a 5.5 ml aqueous solution was
12 used to dissolve 0.06 gram sodium borate decahydrate, and
13 0.6 gram Cabosil M5 silica was slurried into the resulting
14 solution. The reaction mixture was heated in a Teflon cup
15 of a stainless steel reactor at 150°C (302°F) for 17 days
16 without agitation. A crystalline product formed which was
17 isolated and identified as SSZ-42 by its X-ray diffraction
18 (XRD) pattern.

19

20

Examples 5-11

21

Synthesis of SSZ-42

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23 Procedures similar to that of Example 4 was used to prepare
24 SSZ-42 using the materials and amounts shown in Table C
25 below.

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01	<u>TABLE C</u>						
02	Ex.	Template	Borate,	Water,	Cabosil	Temp.	Time
03	No.	mM	gms	ml	gms	°C (°F)	(days)
04	5	A, 16.3	0.38	42	3.26	150 (302)	3
05	6	B, 32	0.80	80	6.0	140 (284)	4
06	7	C, 4.8 1NNaOH	0.11,	13	0.96	150 (302)	18
07	8	A, 53	1.25	143	11.0	150 (302)	4
08	9	A, 2.5	0.17	10	0.75	150 (302)	3
09	10	A, 2.5	0.044	10	0.75	150 (302)	3
10	11	A, 667	22.67	1800	200	150 (302)	5

11 In Examples 5-11, all of the reactions were seeded with
 12 SSZ-42 in the as-synthesized form to the extent of about 1%
 13 of the silica. Examples 6 and 11 were stirred at 100 RPM.

14
 15 The XRD data for the as-synthesized (but not calcined)
 16 SSZ-42 prepared in Example 11 is shown in Table III below.

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TABLE III

	<u>2Theta</u>	<u>d</u>	<u>I/I₀</u>
04	8.219	10.7487	76.3
05	9.707	9.1041	6.1
06	13.641	6.4861	7.3
07	15.272	5.7968	3.2
08	16.033	5.5234	7.9
09	16.475	5.3762	13.6
10	19.125	4.6368	19.6
11	19.497	4.5492	4.2
12	20.597	4.3086	100.0
13	21.544	4.1213	21.0
14	21.760	4.0809	46.0
15	23.873	3.7243	31.8
16	24.337	3.6543	1.8
17	24.903	3.5725	10.5
18	25.349	3.5107	9.0
19	26.211	3.3971	22.3
20	26.751	3.3298	22.1
21	27.428	3.2491	2.5
22	27.704	3.2173	3.0
23	28.371	3.1432	7.7
24	28.934	3.0833	2.2
25	29.407	3.0348	15.3
26	30.185	3.9583	3.1
27	31.310	2.8545	1.6
28	31.784	2.8130	7.9
29	32.406	2.7605	3.1
30	33.315	2.6872	5.2
31	34.024	2.6328	6.1
32	34.721	2.5815	4.2
33	35.437	2.5310	3.4
34	35.777	2.5077	3.5
35	36.150	2.4827	4.3
36	36.477	2.4612	1.4
37	36.878	2.4353	6.8
38	40.599	2.2203	2.5

